THALES Project No: 1190

Investigation of Flattening Mechanism of Molten Droplets during Coating Formation with Plasma Spray Technique

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1. Introduction

Thermal spray coatings are built up by the accumulation of solidified particles (splats) by the deposition of individual molten droplets. Coatings properties such as porosity, adhesion, depend from the splats morphology. It has been proved that for each combination of substrate-powder a characteristic temperature (Ttr) exists. When Ts<Ttr (Ts: the substrate temperature) splashed shape splats are formed and when Ts>Ttr disk-like splats are formed. The coatings adhesion depends from the substrate roughness. Aim of this research program was the study of simultaneous effect of temperature and roughness (Ra) of substrate in the flattening of molten droplets in order to produce thermal spray coatings with improved properties. Further aim was the development of an analytic model, describing the flattening of droplets, that takes into account the substrate roughness. The originality of this project was the study of the simultaneous effect of Ts and Ra of substrate on the flattening of thermally sprayed droplets. Withal, in the present study, industrial spraying conditions were used, so that the obtained results could find direct applications. Furthermore, the set up used for the collection of few splats was original. The research program was made in cooperation with the research team PROCEDE (Maître de Recherche, Dr Michel Jeandin) of Centre des Matériaux P.M Fourt, of Ecole Nationale Supérieure des Mines de Paris.

2. Materials and Processes

The CuAl powders were sprayed under atmospheric conditions (table 1) with Controlled Atmosphere Plasma Spray System (C.A.P.S.) at the Centre for Plasma Processing (Evry, France). In order to collect only few splats, the set-up illustrated in fig. 1 was used. Ts was measured with a K-type thermocouple located at the rear of the specimen.

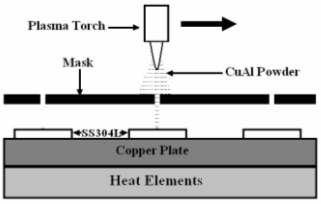

Figure 1: Experimental Set-Up.

Table 1 Spray Parameters

Plasma gas (l/min)	54 Ar, 9 H_2
Intensity (A)	500
Tension (V)	67
Powder feeding rate (g/min)	27
Powder feeding rate (g/min)	27

Coupons of $24x24x3mm^3$ made of SS304L were used as substrate, prepared with different procedures: (i) substrates prepared by grinding with SiC paper and a final polishing with diamond resulting in an average roughness of R_a=0.01-0.03 μm, (ii) substrates grit blasted using 300 μm alumina grit resulting in an average roughness of R_a=1.89-2.43 μm and (iii) substrates grit blasted using 700 μm alumina grit resulting in an average roughness of R_a=4.36-4.98 μm. The substrates were preheated at three Ts: 25°C, 165°C and 270°C. Commercial CuAl (Sulzer-Metco) gas atomized powders were used, with particle distributions of -53+11 μm (51F-NS) and -125+45 μm (51-NS).

3. Results

3.1 Splats Characteristics on Mirror Polished Substrates.

3.1.1 AFM Observations

In the case of fine CuAl powders, the morphology (fig.2) of the splats maintained disc-like by alteration of the Ts. The powder granulometry as well as the addition of small amounts of Al promoted a decrease in Ttr in the region of 25°C [1]. The effect of Ts is more obvious for the coarse powder. The splat morphology changed from fragmented (fig. 2b) to disk-shaped (fig. 2c). For pure cooper it was found that Ttr~200°C [2]. Similarly, the presence of small amounts of Al promoted a decrease in Ttr of coarse CuAl. The flattening degree (ξ=splat diameter/droplet diameter) of the splats produced was calculated by AFM measurements (table 2).

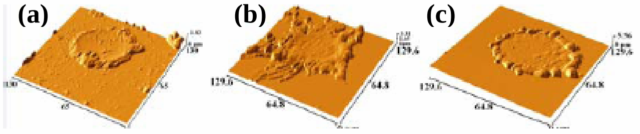

Figure 2: AFM of CuAl splats at Ts: (a) 25°C (51F-NS), (b) 165°C (51- NS), (c) 270°C (51-NS).

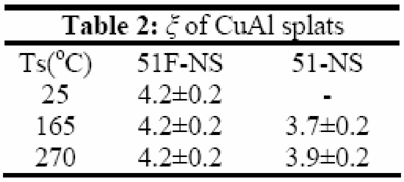

Table 2: ξ of CuAl splats

Ts(°C)	51F-NS	51-NS
25	4.2±0.2	-
165	4.2±0.2	3.7±0.2
270	4.2±0.2	3.9±0.2

3.1.2 SEM Observations

Only for Ts≥165°C signs of oxidation ("black spots"), at the splats surface, were observed (fig. 3b,c). It is confirmed (fig. 3e) that aluminium oxides formed, as the Al peak was the most intensive (fig. 3e) in the EDS analysis. For Ts≥165°C SEM observations showed different appearance of small splats indicating that oxidation was taken place (fig. 3c). Splats were well flattened for all the Ts (fig. 3c).

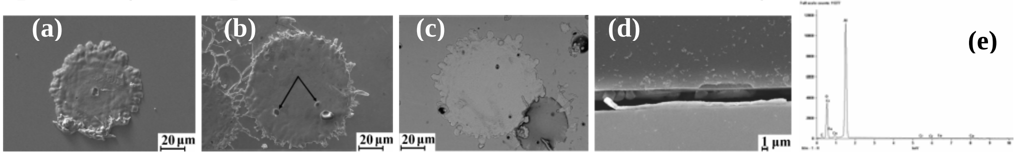

Figure 3: SEM of splats (fine powder) : (a) Ts=25°C, (b) Ts=165°C, (c) Ts=270°C, (d) Ts=165°C (cross section), (e) EDS analysis of "black spots"

In the case of coarse CuAl only for Ts≥165°C splats exhibited superficial isolated aluminium oxides. Splats adhesion on smooth SS304L substrate was not satisfactory (fig. 4b and 4d) for Ts=165°C. In the case of Ts=270°C the contact splat-substrate was satisfactory (fig 4c and 4e). The improved splat-substrate contact for Ts=270°C could be attribute to the slower droplet solidification due to the higher Ts. The slower solidification also explains the higher (ξ) that it was found in the case of Ts=270°C (table 2). Another reason that promoted the improved contact is the possible nm scale roughness, which improves the wettability [3].

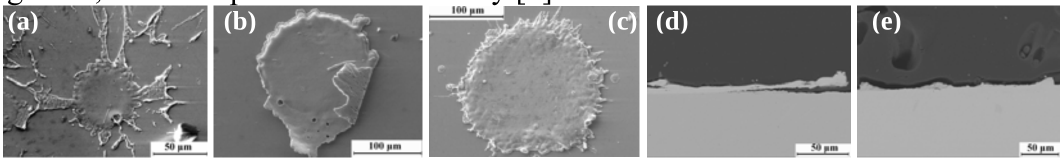

Figure 4: SEM of splats (coarse CuAl): (a) Ts=25°C, (b) Ts=165°C (c) Ts=270°C, (d) Ts=165°C (cross-section), (e) Ts=270°C (cross-section)

3.1.3 EPMA Observations

In the case of fine powder for Ts=25^{o}C, no evidence of oxidation was observed with EPMA. For preheated substrates two kinds of splats were examined, splats with evidence of oxidation (fig. 5a) and splats that did not seem to be oxidized (fig. 5b). In the case of Ts=165^{o}C it is shown (fig. 5a) that smaller particles were oxidized, since the oxygen concentration was ~10% . For Ts=270^{o}C the EPMA (fig. 5b) of the splats presented above (fig. 3c) revealed that only at the small splats, the weight concentration of oxygen was greater than 15%. EPMA was performed in the cross section too in order to investigate if the oxides existed only at the surface. It was found that only in the case of small splats an oxygen concentration of 2.6% was detected near their free surface (fig. 5c). The difference of oxygen concentration between splat surface (fig. 5a) and cross section (fig. 5c) revealed that a sub-micron oxide layer formed in small splats [1].

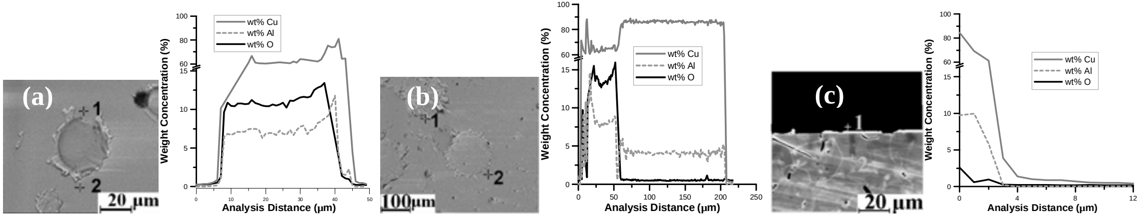

Figure 5: EPMA analysis of splats (51F-NS) at Ts (a) 165^{o}C, (b) 270^{o}C(c) 165^{o}C

In the case of coarse powder the EPMA confirmed the absence of superficial oxide layer on splats formed on pre-heated substrates. For Ts≥165^{o}C after the impingement of the particles on the substrate, due to their large contact area with the substrate, they solidified more quickly compared with the particles of the fine powder and they did not form a superficial oxide layer.

3.2 Splats Characteristics for Grit Blasted Substrates (Ra~1.89-2.43 µm)

3.2.1 SEM Observations

Splats exhibited contiguous shape with fingers. At Ts=25^{o}C splats exhibited pores to their surface and at the interface splat-substrate, due to the asperities, and air pockets trapped underneath the liquid droplets (fig 6a, 6d). Oxidized splats were found at Ts≥165^{o}C (fig. 6c). The substrate roughness prevented scanning of splats using the AFM, therefore the (ξ) of splats was calculated by the splats cross-section. It was calculated that ξ=2.5±0.2 by measuring the diameter and the thickness of the splats, using the mass conservation. The decreasing of (ξ) by increasing of Ra was normal as the spreading of a splat was delayed due to the surface modifications introduced from the grit blasting. Splats/substrate contact was satisfactory on preheated substrates

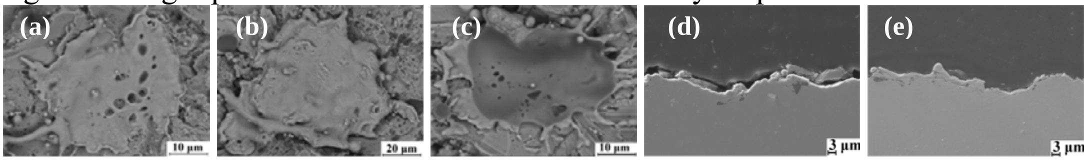

Figure 6: SEM of splats (fine powder) onto SS304L (R_a~1.89-2.43 µm) at Ts (a) 25^{o}C, (b) 165^{o}C, (c) 270^{o}C (d) 25^{o}C (cross section), (e) 270^{o}C (cross section)

In the case of coarse CuAl, extensive splashing was observed for Ts=25^{o}C (fig. 7a) and consequently no further studies made to these splats. On preheated substrates splats exhibited uniform shape with isolated aluminium oxides found on their surface (fig. 7c). The flattening degree was ξ=2.2±0.2 for Ts=165^{o}C and ξ=2.3±0.2 for Ts=270^{o}C. For Ts=165^{o}C the contact splat-substrate was improved as the roughness was increased from R_a~0.01-0.03 (fig. 7b, 7d) μm to R_a~1.89-2.43 μm (fig. 9d,e) [1].

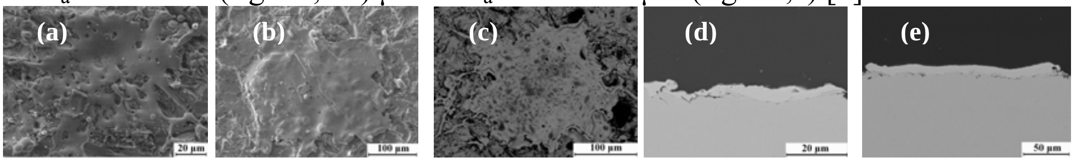

Figure 7: SEM of splats (coarse powder) onto SS304L (R_a~4.36-4.98 μm) at Ts (a) 25°C, (b) 165°C, (c) 270°C (d) 165°C (cross section), (e) 270°C (cross section)

3.2.2 EPMA Observations

Splats formed on substrates at Ts=25°C did not exhibit oxidation. EPMA analysis led to almost the same results for pre-heated substrates. Splats with small diameter (fig.8a), had a weight concentration of 2.2% oxygen on their free surface which corresponds to a sub-micron superficial oxide. Splats with larger diameter have not shown oxidation as is shown in fig. 8b. On the other hand in the case of coarse powder, even at Ts=270°C, it was not observed any existence of superficial oxide (fig. 8c)

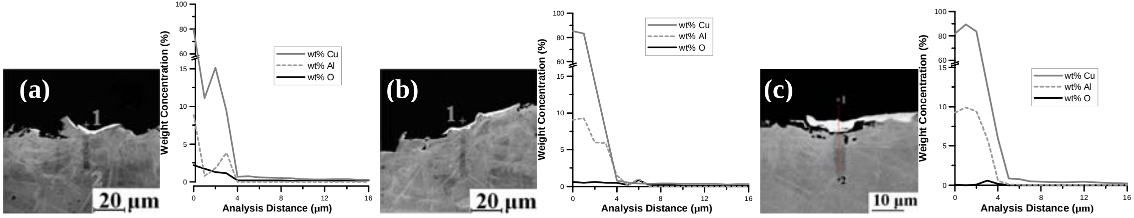

Figure 8: Cross-section EPMA of splats at (a) 165°C (51F-NS), (b) 270°C (51F-NS), (c) 270°C (51-NS)

3.3 Splats Characteristics for Grit Blasted Substrates (Ra~4.36-4.98 μm)

3.3.1 SEM Observations

Splats of 51F-NS were more irregular. Pores were existed on their surface and at the interface splat-substrate only for Ts=25°C (fig. 9a, 9d). It was calculated that ξ=2.1±0.2. For Ts≥165°C oxidized splats were found (fig. 9c) and the contact splat-substrate was satisfactory (fig 9e). For coarse CuAl, splats exhibited contiguous shape with fingers only for Ts≥165°C (fig 10a, 10b). In the case of pre-heated substrates the contact splat-substrate was satisfactory (fig 10c, 10d). It was calculated that: ξ=1.9±0.2 for Ts=165°C and ξ=2.0±0.2 for Ts=270°C

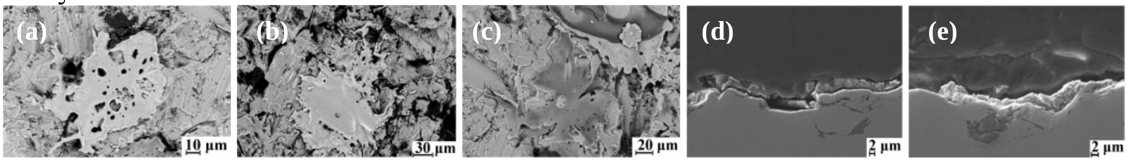

Figure 9: SEM of splats onto SS304L (R_a~4.36-4.98 μm) at Ts (a) 25°C, (b) 165°C, (c) 270°C, (d) 25°C (cross-section), (e) 165°C (cross-section)

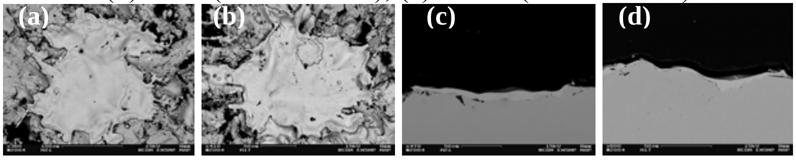

Figure 10: SEM of splats onto SS304L (R_a~4.36-4.98 μm) at (a) Ts=25°C, (b) Ts=165°C, (c) Ts=165°C (cross section), (d) Ts=270°C (cross section)

3.3.2 EPMA Observations

Near the free surface of small splats of 51F-NS an oxygen concentration of 15% was detected (fig. 11a). Comparing figures 8 and 11 it is observed that the oxygen concentration, increased with the increasing of Ra. Other researchers reported [4] that the cooling time decreases with an increase of the Ra. Because of the higher cooling time, a splat remained molten for longer time and consequently a thicker oxide layer was formed. Due to the higher cooling time, in the surface of larger particles a sub-micron oxide layer was formed as an oxygen concentration of 2.4% was detected on their surface (fig. 11b). In the case of splats of 51-NS no evidence of oxidation was observed for all the Ts (fig. 11c)

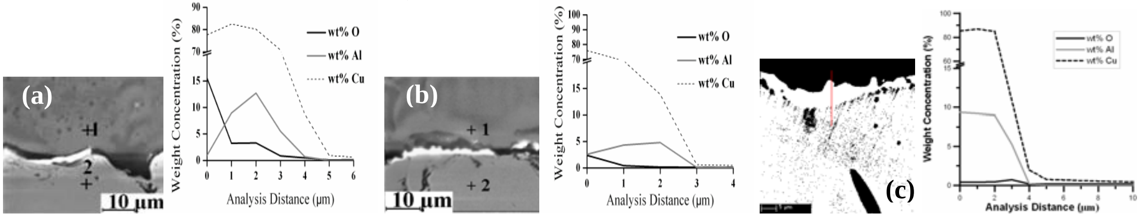

Figure 11: Cross-section EPMA of splat at (a) Ts=165°C (fine powder), (b) Ts=270°C (fine powder), (c) Ts=270°C (coarse powder)

4. New Analytic Model

The analytical model of Zhang [5] was improved in order to consider the surface roughness of the substrate too. The model assumes a molten droplet (initial radius R_0) that impinges perpendicular with velocity (w) on a substrate. The change of (ξ) as function of dimensionless time t′ (t′=wt/R_0) was calculated by Zhang:

$$\frac{d}{dt'}\left[\eta\cdot\dot{\xi}^2\cdot\left(1+\frac{176}{63}\cdot\frac{\eta^2}{\xi^6}\right)\right]+\frac{5}{We}\cdot\frac{d}{dt}\left[\xi^2\left((1-m)+\frac{8}{3}\cdot\frac{\eta}{\xi^3}\right)\right]+\frac{45}{8}\cdot\frac{1}{\eta\cdot\mathrm{Re}}\cdot\xi^4\cdot\dot{\xi}^2\cdot\left(1+\frac{256}{15}\cdot\frac{\eta^2}{\xi^6}\right)=0 \quad (1)$$

where: m is the wetting coefficient, Re is the Reynolds number, We is the Weber number, $\eta=1-(3/4)\cdot\xi^2\cdot\omega\cdot S\cdot(t')^{1/2}$, ω and S are parameters of substrate material. Assuming that the mean surface roughness of the substrate is (ε), equation (1) could be written:

$$\frac{d}{dt}\left[g\cdot\dot{\xi}^2\cdot\left(1+\frac{176}{63}\cdot\frac{\eta^2}{\xi^6}\right)\right]+\frac{5}{We}\cdot\frac{d}{dt}\left[\xi^2\left((1-m)+\frac{8}{3}\cdot\frac{g}{\xi^3}\right)\right]+\frac{45}{8}\cdot\frac{1}{g\cdot\mathrm{Re}}\cdot\xi^4\cdot\dot{\xi}^2\cdot\left(1+\frac{256}{15}\cdot\frac{g^2}{\xi^6}\right)=0 \quad (2)$$

where $g=\left(1-\frac{3}{4}\left(\frac{\xi^2\cdot\varepsilon}{R_0}\cdot\left|\sin\left(\frac{\pi\cdot\xi\cdot R_0}{\varepsilon}\right)\right|\right)+\xi^2\cdot\omega\cdot S\cdot\sqrt{t}\right)$

The (ξ) was calculated by the numerical solution of equation (2) with initial conditions ξ(0)=0 και ξ′(0)=$(5/3)^{(1/2)}$. A characteristic case is presented where it is considered that a particle of powder 51F-NS impinge on a roughened SS304L substrate (Ra~4.36-4.98 µm). For this case, the change of (ξ) as function of dimensionless time (t′) is presented in fig. 12. For the marked values of (t′) (fig. 12) results in the schematically snapshots (fig.13) of the droplet flattening on roughened SS304L.

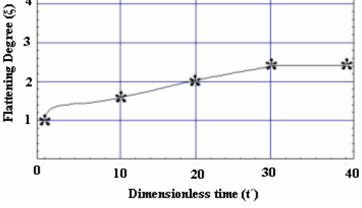

Figure 12: The change of (ξ) as function of dimensionless time (t′)

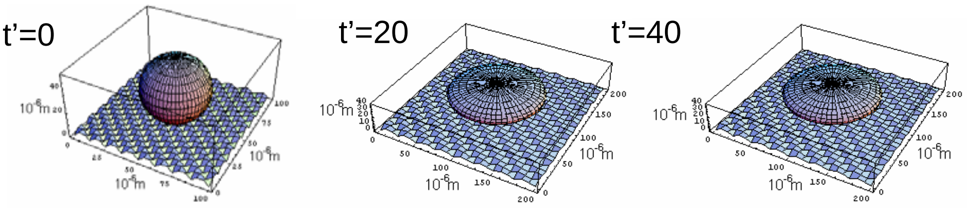

Figure 13: Flattening snapshots of a CuAl (51F-NS) droplet on SS304L (Ra~4.36-4.98 μm)

5. Conclusion

A completed experimental study was presented dealing with the simultaneous effect of temperature and roughness of substrate on the flattening of plasma sprayed droplets under industrial conditions of spaying. The choice of powder, temperature and roughness of substrate for the production of coatings with improved properties should be done with attention. More specifically:

i. The increase of Ts has as result the production of disc-like splats and the improvement of splat-substrate adhesion.
ii. The usage of fine powder has as result the production of splats with better morphology. However the excessive increase of Ts, that promotes the production of splats with optimal morphology could cause undesirable oxidation. The usage of coarse powder demand extremely high Ts, which promotes the formation of disc-like splats with good adhesion, but could cause oxidation on splats or/and on the substrates, as well as development of thermal stresses in the substrates.
iii. The increase of surface roughness, could improve the wetting and consequently splats with better adhesion could form, in lower Ts. However, an extremely increase of roughness could promote the oxidation, the splashing or the appearance of porosity.

Further a new improved analytic model was developed by inserting the effect of the substrate roughness in the model of Zhang. It was observed that the values of (ξ) calculated with this model, are in good agreement with the experimental (ξ).

7. References

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